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The two-letter codes and other abbreviations are explained in the section "Code and Abbreviation Guidance Notes" which is published periodically in the PCT gazette.

(54) Title (English): Polymerization catalyst composition for ethylene oxide and process for production of poly(ethylene oxide) with the same

(54) Title (Japanese): Ethylene oxide polymerization catalyst compositions and a method for the production of poly(ethylene oxide) in which said compositions are used

(57) Abstract: Provided are a polymerization catalyst composition for ethylene oxide which can give poly(ethylene oxide) having a molecular weight lower than that of the prior art and a relatively narrow molecular weight distribution, and a process for the production of poly(ethylene oxide) by the use of the catalyst composition. The catalyst composition makes it possible to produce poly(ethylene oxide) having a molecular weight ranging from about 20,000 to 200,000 through direct polymerization in a high yield with economic advantage, and is characterized by comprising (A) an organoaluminum compound and (B) at least one member selected from among alkali metal alkoxides and alkali metal hydroxides. According to the process, poly(ethylene oxide) having a molecular weight falling within the above range can be produced by the use of the catalyst composition under the same polymerization conditions as those of the prior art.

(57) Abstract (Japanese): There are provided ethylene oxide polymerization catalyst compositions with which it is possible to produce poly(ethylene oxide) of which the molecular weight is low when compared with the conventional methods and of which the molecular weight distribution is within a comparatively narrow range, and a method for the production of poly(ethylene oxide) in which said catalyst compositions are used. The catalyst compositions are compositions with which it is possible to produce by means of direct polymerization in high yield and economically poly(ethylene oxide) polymers which have a molecular weight in the range from about 20,000 to about 200,000, and they are characterized in that they include an

(A) component comprising an organo-aluminum compound and at least one (B) component comprising an alkali metal alkoxide compound or alkali metal hydroxide compound. Moreover, with this method of production it is possible to produce poly(ethylene oxide) polymers within the abovementioned molecular weight range under the same polymerization conditions as with the conventional methods by using a catalyst of the abovementioned catalyst composition.

Specification

ETHYLENE OXIDE POLYMERIZATION CATALYST COMPOSITIONS AND A METHOD FOR THE PRODUCTION OF POLY(ETHYLENE OXIDE) IN WHICH SAID COMPOSITIONS ARE USED

Technological Field of the Invention

This invention concerns catalyst compositions which can be used when polymerizing ethylene oxide (ethylene oxide polymerization catalyst compositions) and a method for the production of poly(ethylene oxide) polymers. More precisely, the invention concerns ethylene oxide polymerization catalyst compositions with which it is possible to produce in high yield poly(ethylene oxide) polymers which have a comparatively low molecular weight and a sharp molecular weight distribution, and a method for the production of said poly(ethylene oxide) polymers.

Background Technology

In the past, polymers of ethylene oxide have been produced in two molecular weight ranges. Those which have a maximum molecular weight of from some 20,000 to some 30,000 are known as "polyethylene glycols". Examples of non-patent literature relating to such materials include "Ring Opening Polymerization" by K.C. Frisch et al., New York, Marcel Dekker (1969) and "Ring Opening Polymerization" by T. Saegusa, Washington, publisher by the Am. Chem. Soc. in 1977.

On the other hand, poly(ethylene oxide) polymers of molecular weight ranging from a few hundred thousand to about 8,000,000 are known as "poly(ethylene oxide)" polymers. The patent literature in which such techniques are disclosed include U.S. Patent 2,971,988 and Japanese Examined Patent Publications 45-7751 and 53-27319.

The literature concerning ethylene oxide polymers is very confusing. There are many cases where the two terms polyethylene glycol and poly(ethylene oxide) are used interchangeably. In fact there is only one index entry in Chemical Abstracts for the ethylene oxide polymers and there is no distinction of fact that they can be produced in just two different molecular weight ranges or of the important difference in that these two types of product are produced using completely different methods.

One of these methods, as mentioned earlier, is a method with which it is possible to produce only material of maximum molecular weight from about 10,000 to about 30,000, while the other method is a method with which it is possible to produce only material of which the minimum molecular weight is above this range, with molecular weight ranging from about 100,000 to 900,000. Hence, it is clear that previously it was not possible to produce ethylene oxide polymers which had a molecular weight in the range of more than about 30,000 but less than about 100,000. If the many applications for polymers which have such an intermediate molecular weight is considered then there is a clearly a considerable demand for this gap in the molecular weight range to be filled.

Furthermore, ethylene oxide polymers in the molecular weight range of a few hundred thousand and above generally have a very wide molecular weight distribution and in fact it is difficult to control the molecular weight during production.

Moreover, it is very difficult to produce economically in high yield ethylene oxide polymers which have a molecular weight above 100,000. The generally known procedure is to reduce by means gamma-ray irradiation the molecular weight of a polymer which has been produced initially with a molecular weight above 1,000,000 to obtain a polymer of the prescribed molecular weight within the range from 100,000 to 900,000.

Consequently, there is a need for ethylene oxide polymers of which the molecular weight is within the range from at least about 10,000 to 30,000, and below about 100,000, the range of molecular weight which has not been achievable in the past. However, up to the present time no catalyst which is suitable for achieving such results has been developed.

The purpose of the present invention is to provide polymerization catalyst compositions with which it is possible to produce economically by means of direct polymerization and in high yield poly(ethylene oxide) polymers which have a molecular weight range from about 20,000 to about 200,000, and a method for the production of poly(ethylene oxide) polymers in which these polymerization catalyst compositions are used.

As a result of a thorough investigation carried out with a view to resolving the problems outlined above, the inventors have discovered that if a specified

polymerization catalyst composition is used when producing poly(ethylene oxide) polymers by the direct polymerization of ethylene oxide then the polymerization of the ethylene oxide proceeds very desirably and the molecular weight distribution becomes very sharp, and the molecular weight of the polymer obtained can be controlled within a specified range, and the invention is based upon this discovery.

Disclosure of the Invention

In this patent application there are disclosed a material composition and a method for the production of ethylene oxide polymers within the range which it has not been possible obtain using either of the production techniques used in the past. The lower limit of the molecular weight range is from 10,000 to 30,000 and the upper limit of the molecular weight range is about 100,000.

Furthermore, the purpose of this patent application is also to disclose a novel catalyst composition comprising two components, which is to say an (A) component and (B) component. When these (A) and (B) components are used together the catalyst system obtained can initiate the polymerization of ethylene oxide effectively and it is possible to produce molecular weights within the prescribed range from about 20,000 to about 200,000 which have a narrow molecular weight distribution, being characterized by a low degree of polydispersion, and it is possible to realize these polymers of ethylene oxide economically by direct polymerization and in high yield.

Furthermore, this patent application also discloses a suitable range which can be used over a wide range.

Optimum Embodiments of the Invention

It has been discovered that certain types of catalyst component can bring about the polymerization of ethylene oxide with very good efficiency. Moreover, it has also been discovered that these polymers have an especially narrow molecular weight distribution and that control of the intended molecular weight can be achieved easily.

The abovementioned catalysts which are used in this invention are generally comprised of two components. The (A) component which is the first component is an organo-aluminum compound. The (B) component which is the second component comprises at least an alkali metal alkoxide compound or alkali metal

hydroxide compound.

Another purpose of the disclosure of the invention is to disclose a method for the production of a certain range of poly(ethylene oxide) polymers. These polymers have a narrow molecular weight distribution and are produced with the novel catalyst compositions disclosed in this application. The catalyst compositions of this invention comprise organo-aluminum compound and alkali metal alkoxide compound or alkali metal hydroxide compound, and either an alkali metal alkoxide compound or alkali metal hydroxide compound can be used individually, or an alkali metal alkoxide compound and an alkali metal hydroxide compound can both be used conjointly, in order to initiate the polymerization of ethylene oxide and to produce the desired poly(ethylene oxide) polymer.

That is to say, the catalyst compositions for the production of poly(ethylene oxide) polymers of this invention are catalyst compositions with which it is possible to produce by means of direct polymerization both economically and in high yield poly(ethylene oxide) polymers which have a molecular weight in the range from about 20,000 to about 200,000, and said catalyst compositions are characterized by including an (A) component, namely an organo-aluminum compound, and a (B) component comprising at least one type of alkali metal alkoxide compound or alkali metal hydroxide compound.

Furthermore, the invention provides a method for the production of poly(ethylene oxide) polymers using a catalyst composition with which the molecular weight can be controlled to the desired molecular weight within the range from about 20,000 to 200,000, and said method is characterized in that a poly(ethylene oxide) polymer of comparatively low molecular weight which has a narrow molecular weight distribution, characterized by having a low degree of polydispersion (degree of polydispersion less than 2.0), is obtained using a catalyst composition which includes an (A) component, namely an organo-aluminum compound, and a (B) component comprising at least one type of alkali metal alkoxide compound or alkali metal hydroxide compound, and in which the proportions the aforementioned (A) component and the aforementioned (B) component in the aforementioned catalyst composition have been controlled.

The poly(ethylene oxide) polymer production catalyst compositions of this

invention will be described first of all.

The (A) component which is included in a catalyst composition of this invention comprises a suitable organo-aluminum compound, and it is a compound which has only Al-C bonds in the molecule. The (A) component does not have any Al-O bonds at all. All of the compounds which include Al-C bonds are encompassed within the scope of the present invention. Suitable organo-aluminum compounds include trimethyl aluminum, triethyl aluminum, tri-isopropyl aluminum, triphenyl aluminum, diphenyl isobutyl aluminum and monophenyl di-isobutyl aluminum, but said compound is not limited these compounds. Tri-isobutyl aluminum is the most desirable of these suitable organo-aluminum compounds. Suitable organo-aluminum compounds ((A) components) include not only individual compounds but also mixtures of more than one type of organo-aluminum compound.

On the other hand, the alkali metal alkoxides of the (B) component include the methoxides, ethoxides, propoxides, butoxides and the like of cesium, rubidium, potassium, sodium and lithium, for example, but they are not limited to just these examples. Form among these potassium t-butoxide is the most desirable.

Furthermore, the (B) component may be an alkali metal hydroxide. Actual examples include lithium hydroxide, sodium hydroxide, potassium hydroxide, cesium hydroxide and rubidium hydroxide, but it is not limited to these examples. From among these alkali metal hydroxides, potassium hydroxide is the most desirable.

Furthermore, the (B) component may comprise a mixture of alkali metal alkoxide and alkali metal hydroxide.

In this invention where a specified catalyst mixture is used, any of the known catalyst additives can be used within ranges such that the polymerization reaction with the effective amount of addition is not impeded. Such substances do not impede the ethylene oxide polymerization reaction when they are used conjointly with a catalyst composition comprising an (A) component and a (B) component. Japanese Patent Application Laid Open 62-232433 can be cited as patent literature in which such a technique has been disclosed.

The effective number of mol of the aforementioned (A) component organo-aluminum compound as a proportion with respect to the aforementioned (B) component alkali metal alkoxide and/or alkali metal hydroxide is at least 3.

The useful concentration of the aforementioned catalyst composition which contains both the aforementioned (A) component and (B) component is from 0.1 to 5.0 mol% Al atom with respect to the ethylene oxide. A concentration of from 0.2 to 3.0 mol% is preferred. The concentration is most desirably in the range from 0.4 to 1.5 mol%.

If the catalyst concentration is less than about 0.4 mol% then the polymerization rate tends to be low. Furthermore, if the catalyst concentration is less than 0.2 mol% then there are cases where the polymerization is unlikely to proceed.

The inventors have not clarified precisely in scientific terms the mechanism of the action of a catalyst composition of this invention, but it is thought that on the one hand the alkali metal ion in the (B) component functions in such a way as to initiate polymerization and the (A) component aluminum atom containing compound acts in such a way that a suitable stereochemical arrangement is adopted in the effective ethylene oxide polymerization. Hence, control of the intended molecular weight of the poly(ethylene oxide) polymer obtained can be achieved effectively by adjusting the mol ratio of the (A) component organo-aluminum compound with respect to the (B) component.

The method for the production of poly(ethylene oxide) polymers in which the aforementioned catalyst compositions are used is described below.

The polymerization of ethylene oxide using a catalyst composition disclosed in the specification of this application can be carried out using known methods which have been published already in connection with other catalyst compositions. Japanese Examined Patent Publications 45-7751 and 53-27319 can be cited as patent citations in which such techniques have been disclosed. For example, either the alkali metal alkoxide or alkali metal hydroxide compound is added initially to a suitable solvent at room temperature in the presence of a water-free inactive gas, such as nitrogen or helium for example. Then the organo-aluminum compound is added to the abovementioned solvent. Finally the required amount of ethylene oxide is added and polymerization is initiated.

Ethers, aliphatic hydrocarbons, aromatic hydrocarbons, halogenated solvents, ketones and the like can be cited as actual examples of suitable known

solvents. In view of the purpose of the invention, two or more of these solvents can also be used conjointly. n-Butane, isobutane, n-pentane, cyclopentane, industrial hexane, n-hexane, isohexane, cyclohexane, n-heptane, n-octane and the like can be cited as the most desirable aliphatic solvents. Hydrophobic solvents of this type are especially desirable. This is because the poly(ethylene oxide) powder produced by the polymerization reaction is easily dried and the powder does not dissolve in volatile organic materials of this type and the powder can be handled without becoming aggregated.

The polymerization reaction of this invention can be carried out over the wide temperature range known in the prior art. Japanese Examined Patent Publications 45-7751 and 53-27319 can be cited as examples of the patent citations in which such techniques are disclosed. However, such a polymerization reaction is preferably carried out within the range from 0 to 50°C. This range is the same as the temperature range used by those in the industry.

Illustrative Examples

The invention is described below by describing examples of production. These illustrative examples are not intended to limit the scope of the invention. In these illustrative examples the terms "parts" and "%" are used on a "by weight" basis. In all of these illustrative examples an inactive gas such as nitrogen, helium or the like was used, and in all cases the reactions were carried out under water-free conditions. Moreover, the degree of polydispersion in the illustrative examples is an index which indicates the molecular weight distribution, and the molecular weights and the molecular weight distributions (degrees of polydispersion) [Mw (weight average molecular weight)/Mn (number average molecular weight)] of the products obtained by polymerization were measured by means of GPC (aqueous system).

Example 1

De-watered n-hexane (200 ml) was introduced into a 1 liter capacity autoclave and 1.0 mmol of potassium t-butoxide was added. Then 10 ml of an n-hexane solution of 1.0M tri-isopropyl aluminum ($\text{Al}(\text{i-Bu})_3$) were added and a polymerization catalyst composition of this invention was obtained.

Subsequently 1.0 mol of ethylene oxide gas was slowly supplied to the

solution in the reactor over a period of 1.5 hours. The reaction temperature was the temperature of the surrounding air (which is to say 25°C).

After the addition of the specified amount of ethylene oxide had been completed the system was stirred for about 2 hours and a slurry of poly(ethylene oxide) powder in n-hexane was obtained.

The slurry obtained in this way was filtered and a powder-like polyethylene oxide powder was finally obtained by drying under reduced pressure conditions.

The yield of this reaction was 99.5%. The molecular weight measured by means of GPC was 40,000 and the degree of polydispersion was 1.28.

Example 2

In this example a reaction was carried out in the same way as except that 2.4 mol, twice the amount used in Example 1, of ethylene oxide was supplied to the reactor.

The yield of poly(ethylene oxide) obtained was 97%. The molecular weight measured by means of GPC was 100,000, and the degree of polydispersion was 1.48.

Example 3

Using the same method as that described in Example 1, the catalyst system was changed by reducing the potassium t-butoxide concentration from 1.0 mmol to 0.6 mmol and changing the amount of 1.0M tri-isobutyl aluminum ($\text{Al}(\text{i-Bu})_3$) n-hexane solution from 10 ml to 6 ml. Then 2.4 mol of ethylene oxide were supplied over a period of 2 hours to the reactor into which the abovementioned catalyst system had been introduced and then the system was stirred for 20 hours.

The slurry of poly(ethylene oxide) in n-hexane obtained in this way was then filtered and the final powder-like product was obtained by drying under reduced pressure.

The yield of this reaction was 70%. The molecular weight measured by means of GPC was 150,000, and the degree of polydispersion was 1.96.

As shown by Examples 1 to 3, the molecular weight of the poly(ethylene oxide) obtained was doubled or trebled respectively when the amount of ethylene oxide used (with respect to the concentration of the catalyst system being used) was doubled or trebled. In the results for these three cases, poly(ethylene oxide) which

had a low degree of polydispersion and which had the prescribed molecular weight could be achieved and controlled at least up to a molecular weight of 150,000 in those cases where a catalyst system of this invention was being used to initiate the polymerization of the ethylene oxide.

Comparative Example 1

Using the same method as described in Example 1, the catalyst system was obtained by using 10 mmol of aluminum isopropoxide ($\text{Al}(\text{OCH}(\text{CH}_3)_2)_3$) instead of using the n-hexane solution which contained 1.0M tri-isobutyl aluminum ($\text{Al}(\text{i-Bu})_3$). On carrying out polymerization using such a catalyst system the yield was no more than 2%. The molecular weight obtained in this way, measured by means of GPC, was 25,000 and the degree of polydispersion was 2.48.

Potential for Industrial Use

The purpose of this invention is to produce poly(ethylene oxide) of comparatively low molecular weight in the form of a solid, granules or powder which is produced by means of the method of this invention. The abovementioned powder-like form has a great advantage over the poly(ethylene oxide) polymers which have been produced by means of the prior art. That is because these are generally wax-like materials with a maximum molecular weight range of from 10,000 to 30,000.

The wax-like materials of the prior art are in practical terms more difficult to handle in given applications such as in thermoplastic processing, for example, than the solid and powder-like materials which have a low degree of polydispersion of this present invention. The polymers of this invention exist in the form of a powder. They can be used alone, or together with other ethylene oxide polymers which have a larger or smaller molecular weight, in a wide range of applications. They can also be used in combination with other water-soluble polymers, partially water-soluble polymers (which is to say so-called combined thickeners which have been hydrophobically modified) and inorganic clay thickeners, and/or water-insoluble thermoplastic polymers.

No limitation is imposed upon the actual examples of such applications but they include paper making, textiles, paints, therapeutic agents, cosmetics, personal gear, toiletries, ceramics, synthetic products, printed products, agricultural products,

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the water industry, the environmental field, the civil engineering and building material fields, electrical applications, mechanical applications, machines and metal processing. The products of this invention are especially useful in therapeutic agents, cosmetics, personal gear and toiletries.

Scope of the Patent Claims

1. A poly(ethylene oxide) polymer production catalyst composition, characterized in that it is a catalyst composition with which poly(ethylene oxide) polymers which have a molecular weight in the range from about 20,000 to 200,000 can be produced economically and in high yield by means of direct polymerization, said catalyst composition including an (A) component, namely an organo-aluminum compound, and a (B) component comprising at least one type of alkali metal alkoxide compound or alkali metal hydroxide compound.
2. The catalyst composition disclosed in claim 1, characterized in that the aforementioned organo-aluminum compound is a compound which has Al-C bonds without having an Al-O bond in the molecule.
3. The catalyst composition disclosed in claim 1 or claim 2, characterized in that the aforementioned organo-aluminum compound is of one type, or of two or more types, selected from among the group comprising the trialkyl aluminum compounds and the tricycloalkyl aluminum compounds.
4. The catalyst composition disclosed in claim 3, characterized in that the aforementioned trialkyl aluminum compound is most desirably tri-isobutyl aluminum.
5. The catalyst composition disclosed in any one of claims 1 to 4, characterized in that the aforementioned alkali metal alkoxide compound is most desirably potassium t-butoxide.
6. The catalyst composition disclosed in any one of claims 1 to 4, characterized in that the aforementioned alkali metal hydroxide compound is preferably potassium hydroxide.
7. The catalyst composition disclosed in any one of claims 1 to 6, characterized in that the aforementioned (A) component is included in an amount of at least 3 mol per 1 mol of the aforementioned (B) component.
8. A method for the production of poly(ethylene oxide), characterized in that it is a method for the production of poly(ethylene oxide) using a catalyst composition with which the prescribed molecular weight can be adjusted within the range from about 20,000 to 200,000, and that in said method a catalyst composition which contains an (A) component, namely an organo-aluminum

compound, and a (B) component comprising at least one type of alkali metal alkoxide compound or alkali metal hydroxide compound, is used, the proportions of the aforementioned (A) component and the aforementioned (B) component in the aforementioned catalyst composition are adjusted, and a poly(ethylene oxide) which has a comparatively low molecular weight which has a narrow molecular weight distribution, being characterized by a low degree of polydispersion, is obtained.

9. The method for the production of poly(ethylene oxide) disclosed in claim 8, characterized in that the mol proportion of the aforementioned (A) component in the aforementioned catalyst composition is adjusted to at least 3 mol per 1 mol of the aforementioned (B) component.
10. The method for the production of poly(ethylene oxide) disclosed in claim 8 or claim 9, characterized in that the amount of the aforementioned catalyst composition used is from 0.1 to 5.0 mol% Al atom with respect to the ethylene oxide.
11. The method for the production of poly(ethylene oxide) disclosed in claim 8 or claim 9, characterized in that more desirably the amount of the aforementioned catalyst composition used is from 0.2 to 3.0 mol% Al atom with respect to the ethylene oxide.
12. The method for the production of poly(ethylene oxide) disclosed in claim 8 or claim 9, characterized in that even more desirably the amount of the aforementioned catalyst composition used is from 0.4 to 1.5 mol% Al atom with respect to the ethylene oxide.